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A NEW FORM OF CATALYTIC PLATINUM

BY
VANDERVEER VOORHEES
B. S. University of Illinois, 1921

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY, IN THE
GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1922

URBANA, ILLINOIS



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UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

June 1 1922

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
SUPERVISION BY Vanderveer Voorhees

ENTITLED A New Form of Catalytic Platinum

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR
THE DEGREE OF Master of Science

Roger Adams

In Charge of Thesis

J. W. Tarr

acting Head of Department

Recommendation concurred in*

Committee

on

Final Examination*

*Required for doctor's degree but not for master's

T H E O R E T I C A L

The Catalytic Process.

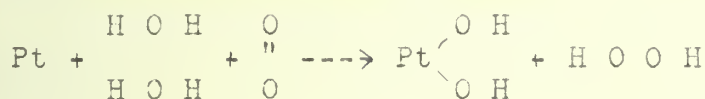
The catalytic activity of platinum was first noticed in 1817 by Edmund Davy when he discovered that a platinum wire induced the combustion of inflammable vapors (methyl alcohol, ether, etc.) at temperatures ^{far} below their kindling point. Later experiments showed that by carefully reheating the wire in air a number of times, the temperature at which it would glow spontaneously could be lowered to 50°C. A practical use and scientific curiosity resulting from the above discovery was Davy's glow lamp, a coil of platinum wire suspended above a volatile, inflammable liquid.

Shortly after this⁽¹⁾ Davy prepared platinum in a very fine state of division by digesting the nitrate (?) with alcohol and obtained essentially the product known as "platinum black." This material was a black amorphous powder having the same catalytic properties as the platinum wire but to a much greater extent. It would ignite an inflammable vapor at ordinary temperature and sometimes explode weakly on heating. Since this time numerous modifications have been made in the method of preparing platinum black, many uses have been found for the material because of its remarkable catalytic activity and many theories have been proposed to account for its peculiar properties, but today after more than a hundred years of diligent research, chemists are still disagreed concerning the processes which give platinum its catalytic power.

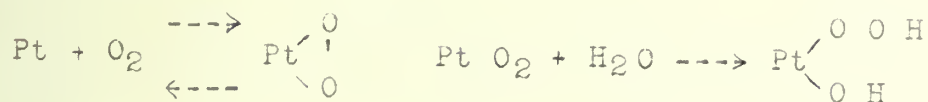
(1) Phil. Mag. (1820) 330

Of the theories advanced for the behavior of platinum black, the two of greatest importance are the adsorption theory and the oxide theory. The former assumes that in the case of oxidation, oxygen condenses or is adsorbed onto the surface of the platinum in which state its concentration might account for the increased chemical activity. In reduction it is the hydrogen which is adsorbed, perhaps as a loose chemical combination from which it is split off in atomic form.⁽¹⁾

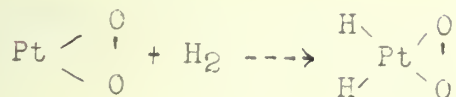
The oxide theory assumes the absorption of oxygen in oxidations to be due to the formation of an oxide of platinum which is then capable of acting as an oxidizing agent. Similarly, reduction is the formation of metallic platinum which has a great affinity for oxygen and hence can act as a reducing agent. The mechanism of this process differs with different authors. Wöhler assumed the formation of hydrogen peroxide as follows:



Willstätter⁽²⁾ has assumed the formation of an oxyperoxide of platinum in oxidation:



and a hydro platinic acid in reduction:



(1) C. C. (1835) 458 Ber. 41, 1984, 1998 (1911)

(2) Ber. (1921) 113

The adsorption theory has many weaknesses. It does not readily explain the reduction of HNO_3 , KClO_3 etc. by dextrose in the absence of hydrogen gas.⁽¹⁾ It encounters great difficulty in explaining the lack of catalytic activity of platinum in hydrogen when entirely freed from oxygen.⁽²⁾ Careful experiments by Mond, Ramsay and Shields⁽³⁾ showed that platinum black contained oxygen, the bulk of which is not liberated until the temperature is raised to 400° . Also, the platinum black would absorb 300 volumes of hydrogen, 200 volumes combined with the oxygen present, and the heat of absorption corresponded with the heat of formation of the water produced, and that the remainder could be removed at 250° . An increase of pressure from 1 to 4 atmospheres has almost no effect on the quantity of either hydrogen or oxygen absorbed. Platinum charged with oxygen absorbs still more on heating to 360° , whereas platinum charged with hydrogen and heated to 360° loses the dissolved gas.

From the above data, the postulation of hydrides of platinum as the active catalyst in reduction seems quite unsupported.

The oxide theory has been assailed by the adsorptionists as unsound on the ground that oxides of platinum do not exist. The great resistance of platinum to oxidation is attested by its use in analytical crucibles etc. where the slightest oxidation would be fatal to accuracy. However, that oxides of platinum do exist has been demonstrated conclusively by numerous investigators. Following are references to the results of some of them:

(1) Bull. Coll. Agr. Tokyo Imp. Univ. 7, 1-6 (1906)

(2) Ber. (1921) 113

(3) Proc. Roy. Soc. 58, 242 (1895)

Topsøe⁽¹⁾ determined the composition and properties of Pt O_2 prepared in the manner of Doebereiner, Wittstein and Fremy. $\text{Na}_2 \text{Pt Cl}_6$ is treated with excess Na O H and on acidification with acetic acid a hydrated Pt O_2 is precipitated. $\text{Pt O}_2 \cdot 4 \text{ H}_2\text{O}$ loses $2 \text{ H}_2\text{O}$ at 100° Prost⁽²⁾ dissolved the above hydrate in H N O_3 and on dilution obtained $\text{Pt O}_2 \cdot 3 \text{ H}_2\text{O}$.

In 1877 Thomsen⁽³⁾ obtained Pt O by boiling potassium chloroplatinite ($\text{K}_2 \text{Pt Cl}_4$) with alkali. It is a strong oxidizing agent, converting formic acid to C O_2 . In the same year, Jorgensen⁽⁴⁾ prepared what he called "platinoxydul oxide" by a sodium carbonate fusion of $\text{Na}_2 \text{Pt Cl}_6$. It is a bluish black powder, stable to aqua regia and heat, and is reduced by hydrogen and by formic acid in the cold, the latter yielding C O_2 . Analysis showed a composition, $\text{Pt}_3 \text{O}_4$.

By heating platinum sponge with $\text{Na}_2 \text{O}_2$ ⁽⁵⁾ a rapid oxidation of the platinum takes place, $\text{Pt}_2 \text{O}_3$ being produced. It is a yellow powder when hydrated but on heating to 450° a dark brown powder results which is only slowly attacked by aqua regia. By electrolysis of fused sodium or potassium nitrates between electrodes of platinum foil, Hittorf obtained yellowish brown and green oxides of platinum.⁽⁶⁾

Electrolysis of an alkaline solution of Pt O_2 between platinum electrodes produces a reddish brown powder at the anode which has

(1) Ber. 3, 462 (1870)

(2) Ber. 19 Ref. 666 (1868)

(3) J. Prakt. Chem. (2) 15, 294 (1877)

(4) J. Prakt. Chem. (2) 16, 344 (1877)

(5) Am. Chem. J. 28, 59 (1902)

(6) C. C. (1848) 23

the formula, Pt O_3 .⁽¹⁾ It is not reduced by H_2O_2 but dissolves in dilute H Cl with evolution of chlorine. It loses oxygen readily, forming Pt O_2 on heating.

In his classic paper on platinum⁽²⁾ Wöhler has shown that platinum black has the property of oxidizing K I to iodine as indicated by the starch test. From its partial solubility in H Cl , he has calculated it to contain 10-18% Pt O . By an oxidation in oxygen gas at 450° Wöhler obtained 44% of platinum sponge converted to platinum oxide. Since platinum black behaves very similarly to Pt O , Wöhler assigns its catalytic properties to this substance.

Willstatter⁽³⁾ has now shown that platinum black used in catalytic reductions is ineffective when deprived of its oxygen, and that catalysis is resumed after the catalyst is exposed to air or oxygen gas. Much work has been done on the poisoning of platinum catalyst and it is seen that most "poisons" are reducing agents.⁽⁴⁾ Platinum poisoned with H C N may be revived by a current of air or oxygen.⁽⁵⁾ The necessity for oxygen is hard to explain on any other assumption than that an oxide of platinum is the active catalyst.

The stability of some of the platinum oxides is quite remarkable. Pt O does not decompose appreciably below 400° . Pt_2O_3 and Pt_3O_4 are stable at higher temperatures than this altho Pt O_2 loses half its oxygen at 280° . Pt O_3 reverts to Pt O_2 on gentle warm-

(1) Ber. 42, 3326 (1909)

(2) Ber. 36, 3475 (1903)

(3) Ber. (1921) 113

(4) Zeit. Physikal. Chem. 37, 1-68 (1901)

(5) Zeit. Physikal. Chem. 37, 551 (1901)

ing altho my experiments show that an oxide higher than Pt O_2 is quite stable at somewhat elevated temperatures. $\text{Pt}_3 \text{O}_4$ retains half its oxygen until a temperature approaching 1000° is reached.

The volatilization of platinum in electric furnaces at comparatively low temperatures followed by crystallization on the cooler portions of the furnace, has been explained by Roberts⁽¹⁾ by the formation of² Volatile oxide at the higher temperature which is unstable at the lower one. This theory is supported by the fact that volatilization does not take place in an atmosphere of hydrogen, nitrogen or in a vacuum. Furthermore a similar phenomenon occurs with the chlorides⁽²⁾ and with the fluorides.⁽³⁾

(1) Phil. Mag. 25, 270 (1913)

(2) Compt. Rend. 947 (1877)

(3) Compt. Rend. 807 (1889)

Preparation and Uses of Platinum Black.*

Many methods have been given for the preparation of platinum black, each claiming an advantage over those previously employed. However, almost all of them have this in common, the precipitation of the platinum from a solution of Pt Cl_4 by a reducing agent in the presence of an alkali.

The first laboratory method for making platinum black was originated by Liebig⁽¹⁾ in 1829. He boiled Pt Cl_2 with $\text{K}_2 \text{C O}_3$ and alcohol, which is essentially the same as the preparation of Pt O as given by Thomsen.⁽²⁾ In 1834 Doebereiner⁽³⁾ reduced Pt Cl_4 with sugar or alcohol in a sodium carbonate solution. Later, Hempel⁽⁴⁾ and also Brunner⁽⁵⁾ reduced Pt Cl_4 in alkali by means of ferrous salts. Mond, Ramsay and Shields⁽⁶⁾ precipitated platinum black from Pt Cl_4 by sodium formate in sodium carbonate. Very active platinum black can be produced by boiling Pt Cl_4 with Rochelle salt⁽⁷⁾ and with glycerol and K O H .⁽⁸⁾ It has also been made by passing hydrogen over $\text{K}_2 \text{ Pt Cl}_6$ at 250° ⁽⁹⁾ and by reduction of Pt Cl_4 with aluminum foil.⁽¹⁰⁾

* Footnote--In German literature platinum black is termed "Platinmohr" from the word Mohr meaning Moor or black.

(1) Pogg. Ann. 17, 102 (1829)

(2) J. Prakt. Chem. (2) 15, 294 (1877)

(3) Ann. 2, 1 (1834)

(4) Ann. 107, 97 (1857)

(5) Ann. 109, 253

(6) Trans. Roy. Soc. 660 (1895)

(7) C. C. (1877) 576

(8) Bull. Soc. Chim. 25, 198 (1876)

(9) Dingl. Polyt. J. CCIV 76

(10) J. A. C. S. 336 (1910)

The most widely used method at present is that of Loew⁽¹⁾ in which he reduced Pt Cl_4 with formaldehyde in the presence of sodium hydroxide. The reduction is incomplete and the platinum black is semicolloidal until it is exposed to air on the filter. Air is absorbed accompanied by a rise of temperature and loss of colloidal nature. Two recent methods are modifications of this last, the object being to facilitate the preparation by avoiding the colloidal form which makes washing and filtering difficult. Feulgen⁽²⁾ shakes the precipitate with acetic acid when it tends to become colloidal. After thoro washing by decantation the black is dried in a vacuum and on exposure to air it absorbs oxygen so rapidly that it glows with the heat of reaction. Willstätter⁽³⁾ conducts the reduction at low temperature and employs K O H which gives the crystalline and relatively coarse $\text{K}_2 \text{ Pt Cl}_6$, thus bringing down the platinum black in particles which permit ready decantation.

Platinum black is finding considerable use in the catalytic reduction of organic compounds and has been used in inorganic reductions and oxidations for some time; N H_3 has been oxidized by air to $\text{N H}_4 \text{ N O}_2$ ⁽⁴⁾ and S O_2 to S O_3 in the "contact process." Nitrogen has been oxidized to H N O_2 ⁽⁵⁾ by air and reduced to N H_3 ⁽⁶⁾ by hydrogen.

(1) Ber. 23, 289 and 45, 1472

(2) Ber. 360 (1921)

(3) Ber. 113 (1921)

(4) Chem. News. 63, 294

(5) Ber. 36, 3479 (1903)

(6) J. C. S. 128, (1881)

Vavon⁽¹⁾ gives a good review of the organic reductions by platinum black. Acetaldehyde, isoamylaldehyde and heptaldehyde yield the corresponding alcohols while acetone, ethyl methyl ketone and diphenyl ketone were reduced to the secondary alcohols.

Palladium black is generally conceded to be a more active catalyst than platinum black and my own experiments have borne this out. However, its action is peculiarly different from that of platinum. While platinum reduces benzene to the hexahydro benzene, palladium reduces it only to the tetrahydro derivative.⁽²⁾ In my experiments I reduced salicylaldehyde rapidly with palladium black to ortho cresol, a product which was never obtained in the use of platinum black under widely varying conditions.

(1) Ann. Chim. Ser. 9, 1, 144

(2) Zeit. Anorg. Chem. 191 (1900)

EXPERIMENTAL

Assuming that the catalytic property of platinum black is due to an oxide, of which it contains only 18-20%, it would appear that the pure oxides of platinum themselves, particularly the higher oxides, would be far more active catalysts than platinum black as usually prepared. Accordingly an oxide of platinum was prepared in the following manner:

1 gm. of platinum was dissolved in aqua regia and the resulting solution was mixed with 10 gm. NaNO_3 . The mixture was rapidly evaporated to dryness and fused over a Bunsen flame in a small porcelain casserole or Pyrex beaker. Between 300° and 400° , red oxides of nitrogen are given off and the platinum is precipitated as a fine powder ranging in color from a light yellowish brown to a dark red-brown. When the evolution of oxides of nitrogen has ceased, the fusion is poured into a cool casserole and allowed to solidify. When cold, it is dissolved in water and decanted twice from the oxide through a filter. The oxide is then transferred to the filter and washed several times until free from nitrates. The powder may be used directly or dried and used at intervals.

All filtrates should be tested for platinum by the method of Wöhler⁽¹⁾. To an acidified portion is added a few drops SnCl_2 sol. A yellow or brown color indicates platinum, the intensity varying with the quantity. The color may be shaken out with ether or ethyl acetate, thus giving a very sensitive test. The filtrates containing platinum

(1) Chem. Zeit. 31, 938 (1907)

should be evaporated and re-fused with a little sodium carbonate which will throw out the platinum quantitatively as a black powder.

Altho this method has not been found in the literature, Jorgensen and Dudley⁽¹⁾ both obtained platinum oxides by fusion methods, and it was thought that fusion with a strong oxidizing agent like Na N O_3 would produce a higher oxide. If a mixture of K N O_3 and Na N O_3 is used in place of Na N O_3 , the fusion point is much lower, but the oxide seems to be in a less finely divided form, since the crystalline, insoluble potassium chloroplatinate is first formed. Consequently the resulting catalyst is less active.

Preparation of the catalyst at different temperatures.

$2\frac{1}{2}$ gram samples of platinum were dissolved in aq. reg. and placed in 50 CC porcelain crucibles with 10 grams of Na N O_3 each. These were heated carefully in an electric resistance furnace, the temperature being controlled by an outside resistance and the fusion being constantly stirred by a thermocouple encased in a Pyrex tube.*

Sample I

<u>Time</u>	<u>Temperature</u>	<u>Remarks</u>
0 min.	----	Placed in furnace
4 "	295°	Fusion
5 "	305°	Evolution of N O_2 begun
25 "	385°	Decomposition almost Complete
35 "	415°	Evolution of N O_2 ceased
40 "	382°	Removed from furnace

(1) loc. cit.

(*) Temperature readings were made by Mr. T. O. Yntema.

Sample II

<u>Time</u>	<u>Temperature</u>	<u>Remarks</u>
0 min.	----	Placed in furnace
9 "	280°	Fusion
13 "	320°	Evolution of N O ₂ begun
20 "	415°	Rapid evolution of N O ₂ . Exothermic
26 "	465°	Decomposition almost complete
32 "	555°	Odor of N O ₂ still noticeable
48 "	504°	Removed from furnace

Sample III

<u>Time</u>	<u>Temperature</u>	<u>Remarks</u>
0 min.	----	Placed in furnace
5 "	290°	Fusion
10 "	425°	Rapid decomposition
23 "	580°	Evolution of N O ₂ practically ceased
29 "	655°	
41 "	680°	Still faint odor of N O ₂
48 "	----	Removed from furnace

After cooling the melts were extracted with water, filtered and washed free from nitrates. The filtrate from No. I showed a considerable quantity of platinum in solution, but No. II and No. III filtrates contained only a trace.

After drying in a dessicator over H₂ S O₄ the three samples were tested for catalytic activity by the reduction of salicyl aldehyde under similar conditions as follows:

.5 gram of the catalyst was placed in a 400 C.C. bottle with 30 gm. salicyl aldehyde and 100 C.C. alcohol. The air was exhausted from the bottle and hydrogen was admitted from an 8 liter tank equipped

with a pressure gauge. The amount of hydrogen absorbed can be closely calculated from the fall in pressure. A drop of 21.3 pounds is equivalent to 1 gm. Hydrogen, and variation of pressure with room temperature was corrected for. The bottle was suspended in a stirrup and oscillated by a motor-driven crank which produced a constant and violent agitation of the contents. After reduction, the alcoholic solution of saligenin was separated from the catalyst, the alcohol distilled off under diminished pressure and the saligenin crystallized from benzene in shining white plates. No attempt was made to obtain the exact yield, the approximate yield being merely a rough check on the experiment.

Sample I

Olive drab amorphous powder.

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
30.0 lbs.	0:00 hrs.	
24.9	0:11	Catalyst black and bottle quite warm
22.0	0:22	
20.7	0:58	
20.6	1:30	
<u>20.6</u>	2:20	

9.4 - Total absorption. (Theory - 10.2)

Catalyst could not be separated by decantation but filtered readily. Yield - 22 gm. saligenin.

Sample II

Slightly lighter in color than I

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
29.9 lbs.	0:00	
28.1	0:30	Catalyst in semicolloidal state. Olive green color.
25.2	0:40	
23.0	0:50	Bottle warm from heat of reaction
21.5	1:00	
<u>19.8</u>	2:17	Catalyst a jet black
10.12 - total absorption		

Catalyst was difficult to separate and had a tendency to pass through the filter.

Yield - 20 gm. saligenin.

Sample III

Slightly lighter color than II

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
29.7 lbs.	0:00	
29.3	0:26	
27.8	0:41	
26.2	0:53	Catalyst an olive green color
21.8	1:53	
20.5	2:33	
<u>19.5</u>	3:43	Catalyst a greenish black
10.2 - total absorption		

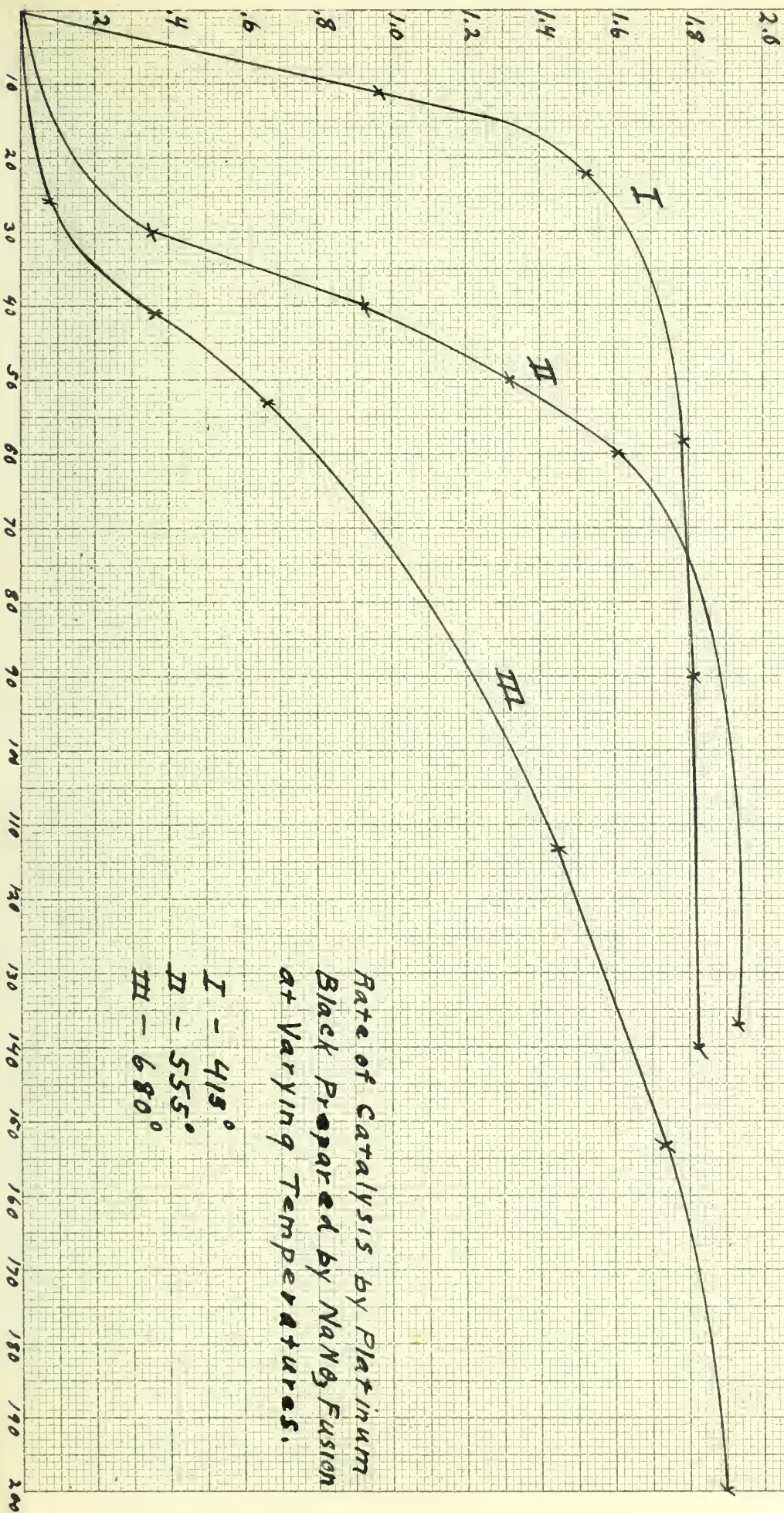
Catalyst did not settle on standing over night. On shaking with a few drops of acetic acid it settled completely in two hours.

Yield of saligenin - 18 gm. (some loss due to oxidation in handling).



Absorption of Hydrogen in Atoms

Time in Minutes



Rate of Catalysis by Platinum
Black Prepared by NaNO₂ Fusion
at Varying Temperatures.

I - 415°
II - 555°
III - 680°

30 grams more salicylaldehyde was added to the above catalyst and a second reduction made to show whether or not its slow action was due to lag at start.

<u>Pressure</u>	<u>Time</u>
30.1	0:00
29.2	0:18
28.9	0:30
27.5	0:51
27.2	1:56
23.3	7:11
<u>20.1</u>	12:26
10.0	

Yield - 16 gm. saligenin.

Analyses of foregoing oxides.

After standing in a dessicator over sulfuric acid for $2\frac{1}{2}$ months, the oxides were analysed by heating in porcelain crucibles at varying temperatures in an electric furnace and finally over a Meeker burner in an atmosphere of hydrogen (Rose crucible) to obtain complete reduction to platinum. Each weighing was made after cooling the crucible in a dessicator in which a vacuum of 1 m.m. was obtained $\frac{1}{2}$ minute after the crucible was removed from the heat.

	I	II	III
Sample	1.9528	2.5708	-----
12 hrs. at 120°	-----	-----	2.3883
Loss of wt. on heating:			
2 hrs. at 120°	.0104	.0220	-----
2 hrs. at 240°	.0323	.0854	-----
2 hrs. at 360°	.0073	.0164	-----

(No change in color)

2 hrs. at 700°	-----	.2410	-----
(dark gray)			
20. min. with Hydrogen	-----	.2523	.4312
		II	III
Percentage loss after heating at 120°		18.9	18.5

Sample II was heated in oxygen over a Meeker burner to constant weight and found to absorb 3.27% of its weight of oxygen and become dark in color. Since Pt O contains 8.16% of the wt. of platinum as oxygen, the above absorption corresponds to a conversion of 40% of the platinum sponge to Pt O, a value very near that obtained by Wöhler from solubility in H Cl.⁽¹⁾

Platinum oxides prepared from various fusion mixtures and their catalytic activity.

Various mixtures were prepared and fused rapidly in porcelain over a Bunsen burner, the temperature being gradually raised to 450° within 5 minutes. The melt was stirred constantly with a pyrometer couple enclosed in a pyrex tube.*

Compositions of mixtures:

I	1 gm. Pt (as Pt Cl ₄)	+	10 gm. Na N O ₃
II	1 gm. "	+	20 gm. "
III	1 gm. "	+	10 gm. " + 2 gm. Na ₂ C O ₃
IV	1 gm. "	+	10 gm. " + .2 gm. Carbon

(1) Loc. cit.

* Temperatures read by Mr. T. O. Yntema

The object of the carbon was to reduce some Na N O_3 to $\text{Na}_2 \text{C O}_3$ after fusion which would cause complete precipitation of the platinum.

Samples I and II were incompletely precipitated.

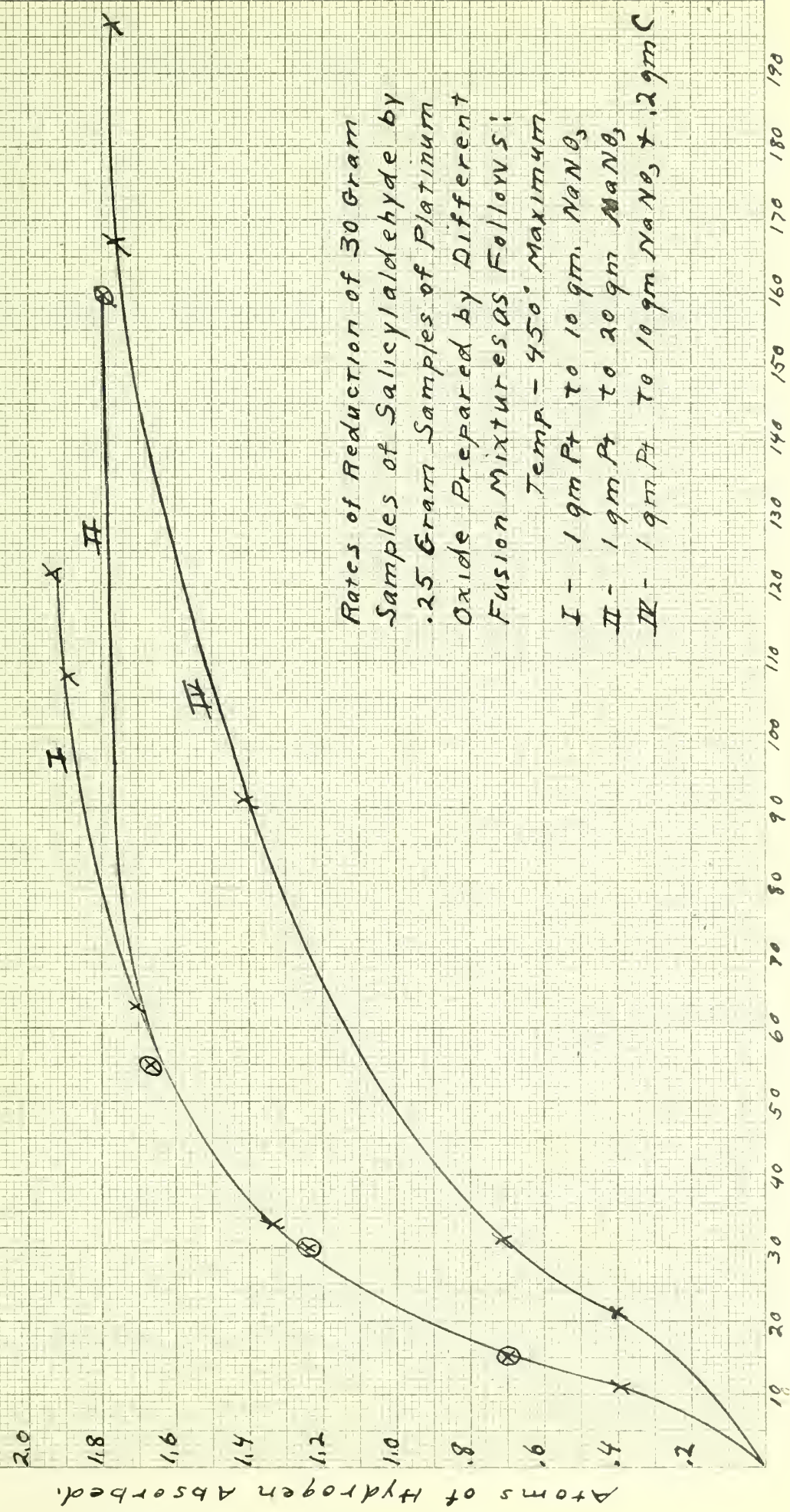
Samples III and IV were almost entirely precipitated.

Samples I and II were a medium brown in color.

Samples III and IV were a light brown and yellow.

The catalysts were tested as follows: 30 gm. salicylaldehyde + 60 C.C. alcohol were shaken with .25 gm. of each catalyst. Results as follows:

	<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
Sample I			
	30.8 lbs.	0:00	
	28.8	0:11	
	23.8	0:33	Bottle warm and catalyst black
	21.9	1:03	
	21.1	1:48	
	<u>20.8</u>	2:02	
	<u>10.0</u>		
Sample II			
	29.6 lbs.	0:00	
	26.2	0:15	Bottle warm
	23.2	0:30	
	21.0	0:55	
	<u>20.1</u>	2:40	
	<u>9.5</u>		
Sample IV			
	30.2 lbs.	0:00	
	28.1	0:21	Bottle warm
	26.4	0:31	
	22.8	1:31	



Rates of Reduction of 30 Gram Samples of Salicylaldehyde by .25 Gram Samples of Platinum Oxide Prepared by Different Fusion Mixtures as Follows:

Temp - 450° Maximum

I - 1 gm Pt to 10 gm NaNO_3

II - 1 gm Pt to 20 gm NaNO_3

IV - 1 gm Pt to 10 gm NaNO_3 + 2 gm C

	<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
Sample IV (cont.)			
	20.9	2:47	
	20.9	3:17	

Qualitative Tests on Brown Oxide of Platinum prepared by Na N O_3

Fusion.

1. The oxide is only partially soluble in boiling dilute H Cl . Insoluble portion dissolves easily in H Br with evolution of Br_2 .
2. It is incompletely soluble in boiling conc. H Cl or aqua regia.
3. It dissolves easily in dilute H Cl on warming with SO_2 to give the yellow chlorplatinic acid.
4. It is only very slightly soluble in 10% Na O H .
5. It is quite insoluble in boiling concentrated H N O_3 .
6. It dissolves easily in constant boiling H Br with liberation of bromine (detected by odor and by shaking out with chloroform). Bromine vapor may be distilled into K I sol. liberating free I_2 . The platinum goes into solution as $\text{H}_2 \text{ Pt Br}_6$ and can be precipitated as the red, slightly soluble potassium salt.
7. The oxide does not change color on treatment with H_2O_2 (3%) either by long standing in the cold or on boiling. It catalyses the liberation of oxygen, however, both cold and hot.
8. On boiling with alcohol in an atmosphere of C O_2 it is reduced to a black powder in 3 minutes. The odor of acetaldehyde is detected.
9. When damp with alcohol and exposed to air the oxide will ignite the alcohol. It will also ignite a mixture of hydrogen and air.

A Comparison of the Catalytic Activity of Platinum Oxide Prepared by Sodium Nitrate Fusion and Platinum Black Prepared by Formaldehyde Reduction.

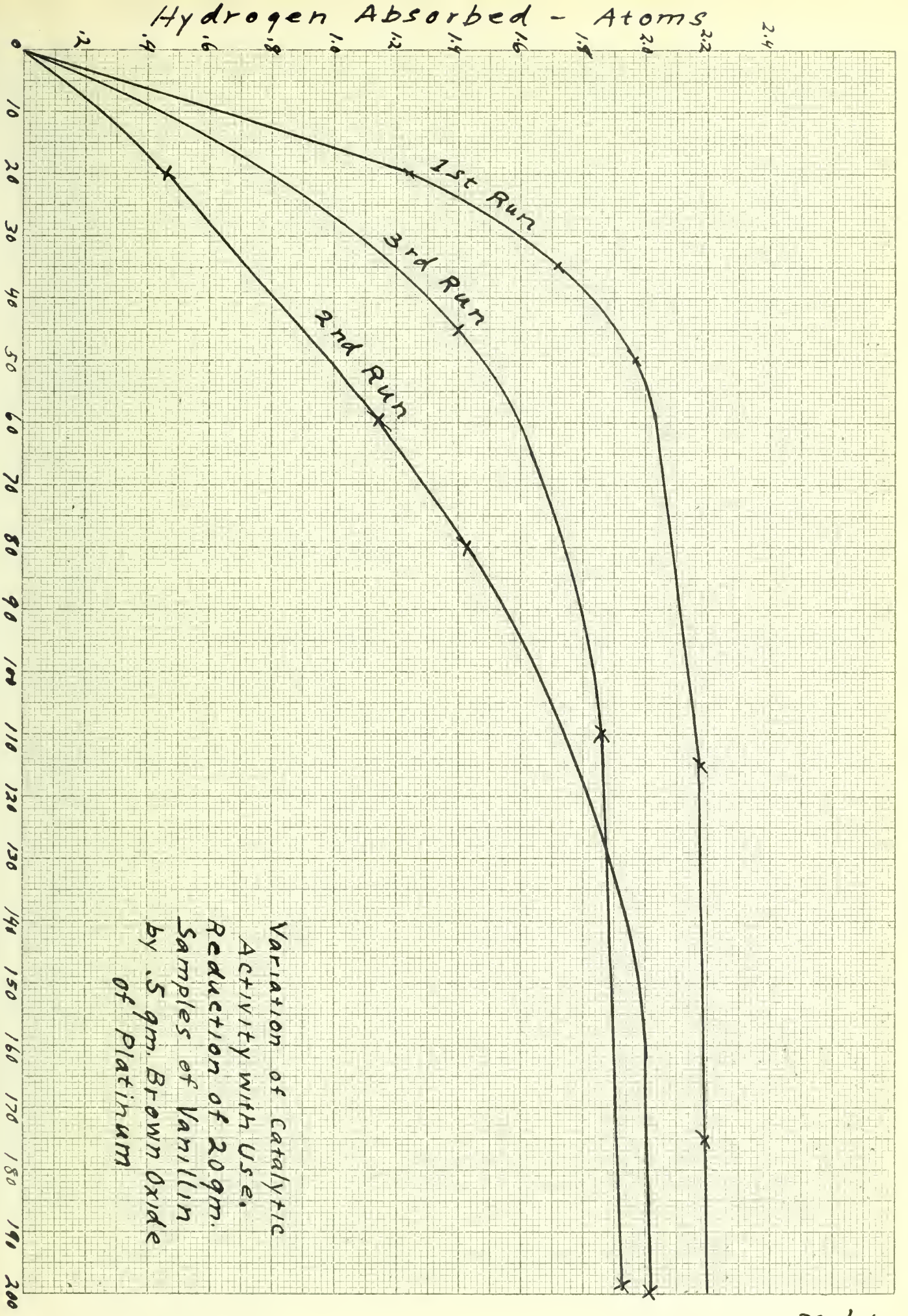
.5 gm. of platinum was converted to the oxide by a Na NO_3 fusion and shaken with 20 gm. vanillin + 100 C. C. alcohol. Using the same catalyst, the reduction was repeated four times to test the wearing quality of the catalyst. Each time the product (Vanillyl alcohol) was decanted from the platinum, the alcohol evaporated under H_2 in. press. and the vanillyl alcohol crystallized from hot water.

	<u>Pressure</u>	<u>Time</u>
First run:		
	23.1 lbs.	0:00 hrs.
	19.6	0:20
	18.3	0:35
Yield - 16.5 gm.	17.6	0:50
M.P. 116° (uncorrected)	17.0	1:55
(Lit. - 115°)	17.0	2:55
	<u>16.8</u>	18:00
Total absorption-6.3 lbs. (Theory 5.5 lbs.)		

Second run:

	25.2 lbs.	0:00
	23.9	0:20
Yield - 16.5 gm.	22.0	1:00
M.P. 116° (uncorrected)	21.2	1:20
	<u>19.4</u>	3:25
Total absorption-5.8 lbs.		

Variation of Catalytic
Activity with Use.
Reduction of 20 gm.
Samples of Vanillin
by .5 gm. Brown Oxide
of Platinum



	<u>Pressure</u>	<u>Time</u>
Third run:		
	22.3 lbs.	0:00
Yield - 18.5 gm.	22.0	0:15
M.P. - 116.5° (uncorrected)	20.7	1:50
	<u>20.5</u>	4:10
	5.4	

Fourth run:		
	25.4 lbs.	0:00
Yield - 15.5 gm.	22.3	0:20
M.P. - 116° (uncorrected)	18.7	1:40
(Probably some leakage)	<u>18.0</u>	3:30
	7.4	

Platinum black was prepared according to the directions of Willstatter⁽¹⁾ as follows:

.5 gm. Platinum as Pt Cl₄ was dissolved in 2 C.C. water to which a few drops of H Cl was added. 3.8 C.C. formaldehyde (33%) was added and the solution cooled in ice and salt. 10.5 gm. 50% F O E was stirred in drop by drop and a yellow paste formed which gradually darkened to a black mush. The mixture was warmed to 60° for $\frac{1}{2}$ hr. and the platinum settled out as a flocculent precipitate. This was washed by decantation four times with 100 C.C. distilled water and the platinum black washed free from water by alcohol. Still wet with alcohol it was placed in the reduction bottle with 20 gm. Vanillin + 100 CC alcohol.

(1) Ber. 113 (1921)

<u>Pressure</u>	<u>Time</u>
25.8 lbs.	0:00 hrs.
25.2	1:45
24.8	3:00
24.4	6:15
24.1	18:45

.4 gm. platinum oxide prepared by Na N O_3 fusion
now added

23.1 lbs.	0:00
21.5	0:45
20.8	1:55
20.0	3:40
17.6	20:10

$\frac{1}{2}$ gm. platinum black was prepared by the method of Feulgen⁽¹⁾

In this method the platinum is precipitated by formaldehyde and Na O H and the colloidal black caused to settle by shaking with dil. acetic acid. After drying in a dessicator over $\text{H}_2 \text{ SO}_4$ it was shaken with 20 gm. vanillin in 100 C.C. alcohol.

<u>Pressure</u>	<u>Time</u>
26.6 lbs.	0:00 hrs.
25.8	3:00
25.4	30:00
25.4	35:00
24.8	42:00

.2 gm. platinum prepared by Na N O_3 fusion now
added

	25.7	0:00
Bottle warm from heat of reaction	18.0	0:30
	17.9	1:05

(1) Ber. 360 (1921)

Catalysis by Pt O

Pt O was prepared by the directions of Wöhler⁽¹⁾ by boiling potassium chloroplatinite with a slight excess of sodium carbonate. 1.06 gm. $K_2 Pt Cl_4$ was dissolved and boiled with $Na_2 CO_3$. Pt O was precipitated as a fine black powder, washed thoroughly with hot water and dried over $H_2 SO_4$. On shaking in hydrogen with 20 gm. vanillin in 100 CC. alcohol, the following results were obtained:

<u>Pressure</u>	<u>Time</u>
25.7 lbs.	0:00 hrs.
23.6	8:25
<u>22.7</u>	27.45
3.0	

.4 gm. platinum prepared by $Na NO_3$ fusion now added

	20.5 lbs.	0:00 hrs.
Pressure drop required by theory - 5.5 lbs.	17.8	0:55
	<u>17.8</u>	6:35
	2.7	

Pt O was prepared after the manner of Thomsen⁽²⁾ as follows: 1.06 gm. $K_2 Pt Cl_4$ containing .5 gm. platinum was dissolved and to it was added the calculated quantity of .1 N. $Na OH$ to precipitate Pt O. on boiling, the Pt O was precipitated and washed by decantation until free from the neutral $Na Cl$ solution. It was shaken in hydrogen with 30 gm. salicylaldehyde in 100 C.C. alcohol with the following results:

(1) loc. cit.

(2) loc. cit.

<u>Pressure</u>	<u>Time</u>
29.5 lbs.	0:00 hrs.
28.0	2:15
25.7	17:35

.2 gm. platinum prepared by Na N O₃ fusion now added

3.8	
22.7 lbs.	0:00 hrs.

Required absorption (Theoretical) 10.2 lbs.

14.8	1:50
<u>14.8</u>	8:05
7.9	

Reduction of Ethyl methyl ketone.

80 gm. redistilled ethyl methyl ketone were shaken with .525 gm. of red-brown platinum oxide from Na N O₃ fusion which had been washed with alcohol and ether previous to use.

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
45.5 lbs.	0:00	
37.0	0:15	Bottle quite warm
32.0	0:20	Pressure increased
13.5		
49.0	0:20	
15.5	1:45	Pressure increased
33.5		
40.0	1:45	
33.0	16:45	
7.0		

33.0 lbs. - total absorption (45 lbs. - theory)

Yield - 74 gm. sec. butyl alcohol - 98° - 101°

Reduction of Phenol.

62 gm. redistilled phenol was dissolved in 50 C.C. alcohol and shaken with .65 gm. ~~brown~~platinum oxide with the following results:

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
31 lbs.	0:00 hrs.	
15	0:40	Pressure increased
16		
47	0:40	Bottle very warm
10	1:50	Pressure increased
37		
50	1:50	
22	6:30	Pressure increased
28		
40	6:30	
28.9	21:10	

11.1

92.1 - total absorption (Theory - 85)

Small amount of unreduced phenol shaken out with Na OH.

Yield - 54 gm. - 156° - 7° Cyclohexanol.

Reduction of Benzamid.

30 gm. benzamid were dissolved in 100 c.c. glacial acetic acid and shaken in hydrogen with .5 gm. brown platinum oxide.

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
39.3 lbs.	0:00 hrs.	
38.6	0:25	Catalyst turned black.
35.3	5:15	
33.8	18:30	
5.5		No product isolated.

20 gm. benzamid dissolved in 100 c.c. warm alcohol and shaken with catalyst from above.

<u>Pressure</u>	<u>Time</u>
30.4 lbs.	0:00 hrs.
23.4	3:30
20.7	7:30
18.5	22:30
<u>18.5</u>	28:00

Yield - 9 gm. hexahydro benzamid crystallized from alcohol. Shining white plates M.P. 185°. (Lit. 185 - 6°)

Reduction of Heptaldehyde.

25 gm. heptaldehyde dissolved in 50 c.c. alcohol was shaken with .5 gm. brown platinum catalyst in hydrogen.

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
30.0 lbs.	0:00	Catalyst became black instantly
29.0	1:25	
1.0		
		.5 gm. more catalyst added.
22.4	0:00	
17.3	1:30	
16.2	7:00	
<u>16.2</u>	17:00	
6.2		
<u>1.0</u>		

7.2 total absorption (theory 9.3)

Yield 22 gm. heptyl alcohol 173°- 175°

Palladium

15 gm. palladium was dissolved in aqua regia and fused with 10 gm. Na N O₃ at about 550°. The precipitated palladium was filtered off and washed free from nitrates, the filtrate showing a considerable quantity of unprecipitated palladium. The catalyst, which was a dark reddish brown and showed a metallic glint in suspension, was placed in the shaking bottle with 30 gms. salicyl aldehyde and 100.cc. alcohol.

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
32.0 lbs.	0:00	
29.0	0:06	Catalyst blackened in a few
25.5	0:16	seconds. Gathered into flocks
16.9	1:10	which settle at once on stopping
14.6	1:53	shaker.

17.4 total absorption. (Theory for saligenin - 10.2)

No saligenin could be isolated from the reduction product, but 14 gm. ortho cresol was obtained, 185°- 187° which could be easily crystallized. A high boiling, syrupy residue remained, probably a condensation product.

A second run was made using the same catalyst.

<u>Pressure</u>	<u>Time</u>	<u>Remarks</u>
29.0	0:00	
27.8	0:18	Shaken with air 18 min.
1.3		
26.0	0:00	
21.1	1:22	
18.4	2:39	
13.3	17:17	

12.7

14.0 - total absorption. Yield - 9 gm. pure o cresol.

In these experiments .2115 gm. palladium was used.

The brown palladium oxide showed the same chemical properties as that of platinum, partial solubility in aqua. regia but soluble in H Br only on warming.

Iridium

$\frac{1}{2}$ gm. of insoluble material obtained from platinum scrap assumed to be iridium was shaken with 25 gm. cinnamic acid dissolved in 100 c.c. alcohol. 10 lbs. of hydrogen was absorbed in 2 hrs. and 20 min. A mixture of liquids was obtained and a small amount of dihydro cinnamic acid was isolated M.P. 48.5 (Lit. - 48.7)

C O N C L U S I O N

The results of the experiments tabulated here seem to indicate that the brown amorphous powder obtained when Pt Cl_4 is fused with Na N O_3 , is an oxide of platinum having a higher oxygen content than Pt O_2 .

Its catalytic activity is apparently due to a lower oxide which is formed in the reduction bottle, (probably Pt O). Its superior activity to Pt O is likely due to physical form (state of division), and its superiority over platinum black is probably due to a larger oxide content and to a gradual reduction of the higher oxide to the active form which sustains the catalysis.

Its ease of preparation and convenient application should commend its use in place of platinum black, the preparation of which is quite difficult if an active form is to be obtained.

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